Endocrine disrupting chemical emissions from combustion sources: diesel particulate emissions and domestic waste open burn emissions

Sukh Sidhu[a,*], Brian Gullett[b], Richard Striebich[a], Joy Klosterman[a], Jesse Contreras[a], Michael DeVito[c]

[a]Environmental Engineering, University of Dayton, 300 College Park, Dayton, OH 45469, USA
[b]National Risk Management Research Laboratory (E305-01), US Environmental Protection Agency, Research Triangle Park, NC 27711, USA
[c]National Health and Environmental Effects Research Laboratory (MD-74), US Environmental Protection Agency, Research Triangle Park, NC 27711, USA

Abstract

Emissions of endocrine disrupting chemicals (EDCs) from combustion sources are poorly characterized due to the large number of compounds present in the emissions, the complexity of the analytical separations required, and the uncertainty regarding identification of chemicals with endocrine effects. In this work, multidimensional gas chromatographic-mass spectrometry (MDGC-MS) was used to characterize emissions from both controlled (diesel engine) and uncontrolled (open burning of domestic waste) combustion sources. The results of this study suggest that, by using MDGC-MS, one can resolve a much greater percentage of the chromatogram and identify about 84% of these resolved compounds. This increase in resolution helped to identify and quantify various classes of polycyclic aromatic hydrocarbons (PAHs) in the combustion emissions that had not been identified previously. Significant emissions (when compared to industrial sources) of known EDCs, dioctyl phthalate (over $\sim$2,500,000 kg year^{-1}) and bisphenol A (over $\sim$75,000 kg year^{-1}) were estimated from uncontrolled domestic waste burning. Emissions of several suspected EDCs (oxygenated PAHs) were observed in both diesel soot and the uncontrolled domestic waste burn samples. The emission rates of known and suspected EDCs estimated in this study suggest that combustion emissions need to be characterized for EDCs to further assess its importance as a source of EDC exposure.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: Bisphenol A; Diesel emissions; Open barrel burning; Oxygenate PAHs; Multidimensional GC-MS

1. Introduction

In recent years, several studies have been conducted to investigate the potential threat of endocrine disrupting chemicals (EDCs) to wildlife and humans (Colborn and Clement, 1992; Colborn et al., 1993; Guillette et al., 1995). It is now known that several natural and man-made EDCs act as mimics or antagonists of endogenous hormones (Crews et al., 1995; Cummings and Metcalf, 1995; Soto et al., 1995). These concerns have led to the initiation of a significant number of in vitro and in vivo studies of the toxicology of EDCs, including the

---

*Corresponding author. Tel.: +1 937 229 3605; fax: +1 937 229 2503.

E-mail address: sidhu@udri.udayton.edu (S. Sidhu).

development of a comprehensive screening procedure to detect potential EDCs (Arnolds et al., 1996; Routledge and Sumpter, 1996; Zacharewski, 1997). Despite these investigations, the extent to which EDCs can negatively impact human and animal health is a subject of debate (Stone, 1994). Most of these EDC studies have thus far focused on commercial chemicals that may be "widely" distributed in the environment (Crews et al., 1995; Cummings and Metcalf, 1995; Harris et al., 1997; Soto et al., 1994, 1995) primarily via aquatic media. Little attention has been directed toward identifying or characterizing other potentially important sources of EDC emissions.

Given the large variety of complex emissions from combustion processes, it is reasonable to expect presence of EDCs as combustion byproducts. For the past two decades, numerous studies have been conducted to investigate the origin and formation mechanism of toxic combustion by-products (Dellinger et al., 1991; Fiedler, 1993; Gullett et al., 1994; Konduri and Altwicker, 1994; Lenoir et al., 2001; Oppelt, 1986; Sidhu et al., 1995). These studies have shown that known EDCs such as polychlorinated dibenzodioxins and furans (PCDDs/Fs), alkylphenols, phthalates, styrenes, polychlorinated biphenyls (PCBs), and polybrominated biphenyls (PBBs) are present in emissions from various combustion processes (Fiedler, 1993; Oppelt, 1986). Along with these known EDCs, several hundred other chemicals are also present in combustion emissions (Ryan et al., 1996). The complexity of the combustion emissions has resulted in the identification of only a small percentage of chemicals emitted, even though considerable effort has been expended to characterize emissions from some combustion sources (Rogge et al., 1993; Schauer et al., 1999).

An examination of Fig. 1, a high-resolution chromatogram of the semi-volatile (C_6 to $\sim C_{16}$) fraction of the emissions collected from a hazardous waste incinerator shows that $\sim 1\%$ of chemicals can be identified because only 10–15% of the chemicals are chromatographically resolvable (Ryan et al., 1996). The exact pattern of the chromatogram may vary among combustion sources, but the general pattern, complexity, and lack of resolution are similar. Initial results suggest that, by using multidimensional gas chromatographic-mass spectrometry (MDGC-MS), a greater percentage of the chromatogram can be resolved and identified (Rubey et al., 1999; Striebich et al., 2002). The majority of the chemicals resolved and identified with MDGC-MS were semi-polar oxygenates that have many structural similarities with known EDCs. The existence of these chemicals in combustion emissions was previously unknown; however, an understanding of combustion processes suggests that all thermal and combustion processes may possess the appropriate conditions and reactants to produce these chemicals (Lenoir et al.,
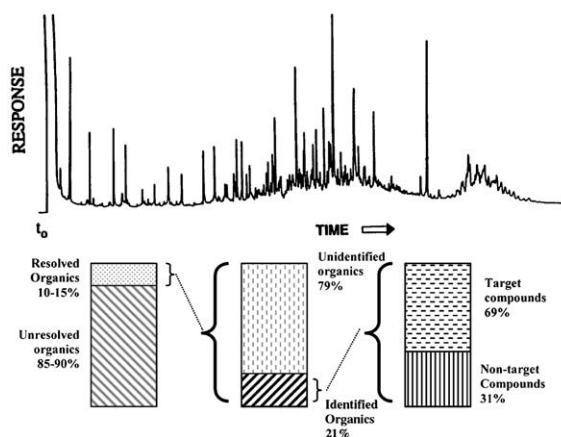

Fig. 1. Chromatogram of the semi-volatile fraction of the effluent from a hazardous waste incinerator collected with a MM-5 sampling train. This sample was subjected to methylene chloride extraction and HRGC-MS analysis using a $50\,m \times 0.2\,mm \times 0.3\,\mu m$ dimethylsiloxane open tubular column.

2001). In fact, these chemicals are probably formed in the post-flame and cool zone of combustors by a surface-catalyzed mechanism similar to that responsible for the formation of PCDDs/Fs in combustion systems (Lenoir et al., 1998; Sidhu, 1999). Thus, these oxygenated and halogenated EDCs may be emitted from essentially any combustion or thermal process.

For this study, samples were collected and analyzed from both controlled and uncontrolled combustion sources. For controlled combustion emissions, diesel particulate samples were selected because of their known environmental and health impact (Harrison et al., 1997; Venkataraman and Friedlander, 1994). In a recent study, Taneda et al. (2002) showed that both estrogenic and antiestrogenic compounds exist in diesel exhaust particles. Also, Watanabe and Oonuki (1999) recently reported that exposure to diesel exhaust can increase the serum testosterone and estradiol levels. Diesel exhaust has also been found to affect the regulation of testicular function in male rats (Tsukue et al., 2001). The results of these studies indicate the need to identify compounds on diesel particulates that are causing estrogenic and antiestrogenic activity. Mori et al. (2002) identified 4,6-dimethyldibenzothiophene (isolated in the neutral portion of a hexane extract) as one of the compounds responsible for estrogenic activity. It seems likely that more than one class of compounds is responsible for the endocrine disrupting behavior of diesel particles, since hexane, benzene, dichloromethane, and methanol extracts of diesel particles showed estrogenic and anti-estrogenic activity (Mori et al., 2002; Taneda et al., 2002; Tsukue et al., 2001; Watanabe and Oonuki, 1999). However, other potential classes of EDC compounds in diesel particle extract have yet to be identified.

The second combustion emission sample analyzed in this study was collected from uncontrolled burning of domestic waste (Gullett et al., 2001; Lemieux, et al., 2000). One survey indicated that 40–50% of rural Illinois residents burn at least a portion of their domestic waste in barrels (Lemieux et al., 2000). The Environmental Protection Agency (EPA) has estimated that approximately 8×10^9 kg of domestic waste per year is disposed through backyard barrel burning (Gullett et al., 2001). A study by the EPA concluded that the PCDD/F emissions from open burning are several orders of magnitude higher than for controlled combustion in a modern, clean-operating municipal waste combustor (Gullett et al., 2001; Lemieux, et al., 2000). Also, the emissions from open burning of domestic solid waste are released at ground level which results in decreased dilution by dispersion. A burn barrel provides poor combustion conditions (low combustion temperature, poor gas-phase mixing, and oxygen-starved conditions) which lead to formation of products of incomplete combustion (Lemieux, et al., 2000). Significant emissions of chlorobenzenes, chlorophenols, polychlorinated biphenyls, and PAHs were also observed from open burning of domestic solid waste (Lemieux, et al., 2000). Presence of the above-mentioned pollutants, bad combustion conditions, and composition of domestic waste (plastic, paper and wood) suggests that uncontrolled domestic waste burning may be a source of EDCs or suspected EDC emissions.

This paper will not only discuss emissions of known combustion EDCs, but also the potential or suspected EDCs that might be present in the diesel and uncontrolled domestic waste burning samples.

2. Experimental

Diesel particle extracts obtained from the Desert Research Institute (DRI) and EPA National Risk Management Research Laboratory (EPA-NRMRL) and emissions from uncontrolled burning of domestic waste were analyzed in this work. The DRI diesel particle extract was prepared by extracting diesel particles (collected during cold-start-0 °C diesel dynamometer tests) in acetone using a microwave extraction technique (Zielinska and Sagebiel, 2001). The second diesel particle extract was obtained from the EPA's on-road diesel emission sampling program using dichloromethane with a soxhlet extraction technique (Gullett and Ryan, 2002). The uncontrolled domestic waste burn sample was generated by burning a variety of household garbage including shoes, food packaging, and non-recyclable plastics in a 55 gal steel drum (Gullett et al., 2001). The sample was collected on a filter/polyurethane foam/filter combination, extracted with methylene chloride via the soxhlet extraction procedure, and then

concentrated to enhance sensitivity (Gullett et al., 2001). To ensure the quality of data, field blank samples were collected during all three of the above-mentioned studies.

Both the diesel and uncontrolled domestic waste burn samples were analyzed using an MDGC-MS technique. MDGC-MS uses multicolumn chromatographic selectivity to separate compounds using a megabore and microbore open tubular column assembly. An in-line cryogenic procedure is used to transfer organics between the two columns. The separated solutes are eventually detected by quadrupole or ion-trap mass spectrometry. This trap-and-release process employs a secondary
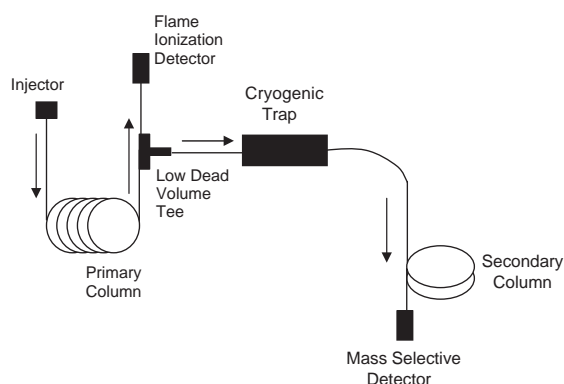

Fig. 2. Simplified schematic of the multidimensional GC-MS system.

Table 1
Experimental conditions for MDGC-MS

Primary column	Secondary column
MTX-5 (Restek, Inc.)	RTX-200 (Restek, Inc.)
30 m length	3.8 m length
0.53 mm internal diameter	0.10 mm internal diameter
1.0 μm film thickness	0.1 μm film thickness
3.0 psi inlet pressure (constant P)	Near atmospheric inlet pressure
25 cm s^{-1} linear velocity (40 °C)	25 cm s^{-1} linear velocity (40 °C)
Initial oven temperature 40 °C	
Initial oven hold time 40 min	*Cryotrap*
Oven programming rate 2 °C min^{-1}	Cooling by conduction
Final temperature 300 °C	Trap temp at initial oven temp −40 °C
Final hold 10 min	Time for actuation of column 45 s
Splitless injection	*Mass selective detectors*
Sample size 2 μl	50–300 amu
	70 eV scanning mode

separation that is independent from the primary separation (thus, *multidimensional* chromatography). The MDGC-MS setup used in this study is similar to the design employed by Marriot and Kinghorn (1997) and has been described in detail elsewhere (Kinghorn and Marriot, 1998; Striebich et al., 2002). The system for this study differed from previous instruments in that the column was moved in and out of a cryogenic zone rather than the zone moving over the column. A simplified schematic of the system is provided in Fig. 2.

The extracted samples from both combustion sources were introduced into a conventional split/split-less injector operated at 280 °C. The primary separation was performed using a megabore stainless-steel column, (RESTEK MTX-5) 30 m, 0.53 mm internal diameters, and a 1.0 μm film thickness. This non-polar column was operated to provide the best possible resolution between

solute zones using conventional flow rates and temperature programs as described in Table 1. After separation in the primary column, each chromatographic zone was processed through a cryogenic trap and quickly released onto the polar secondary column. In the trap, primary column effluents were subambiently (−60 °C) refocused into a narrow band of solute and then released into the remainder of the polar secondary column. By allowing effluent to collect at the front of the trap (inside the secondary column) and then pulling the column out of the cryogenic zone, the solutes were trapped effectively and quickly released. The separation in the secondary column was essentially isothermal over the 45 s analysis time. At the completion of the secondary separation, the components of the sample were detected using a mass selective detector (MSD). Experimental conditions for the secondary column and detector are listed in Table 1.
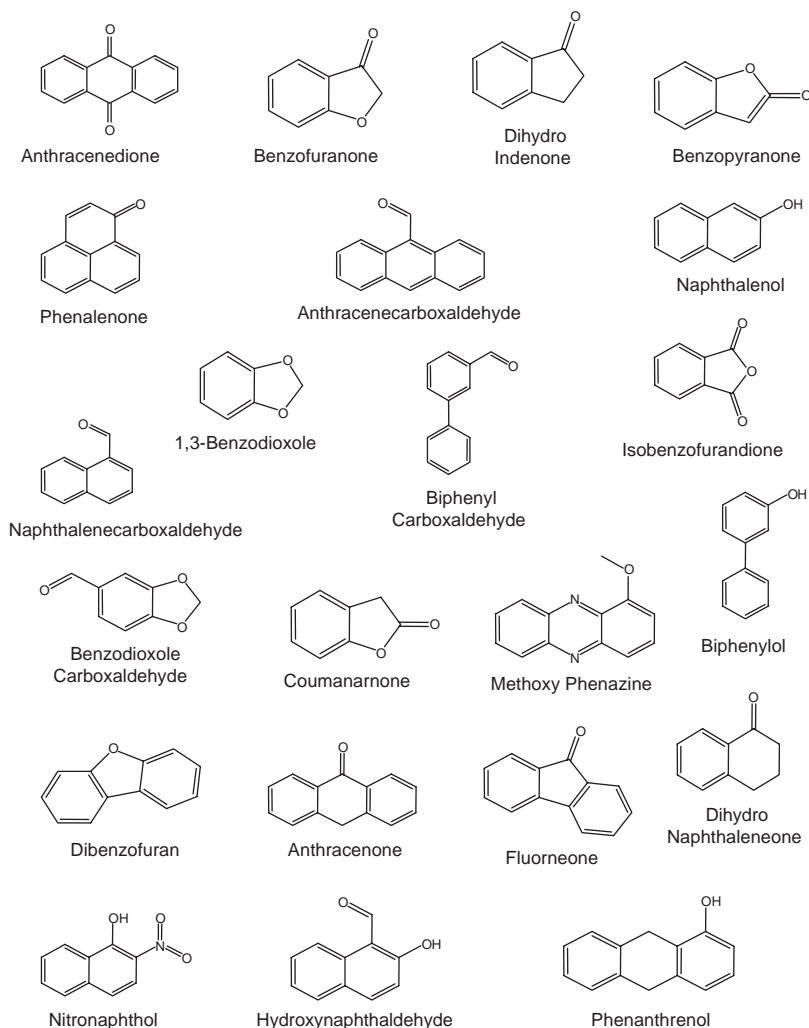

Fig. 3. Oxy-PAHs identified by MDGC-MS in the diesel particulate extract samples.

The enhanced separation achieved by MDGC technique generated chromatograms with hundreds of peaks. The chromatographic peaks thus generated were identified (after background subtraction) using automated search routines. Once the peaks were integrated and library reports were generated, the library hits were matched to the areas by peak number and retention time. All peaks that had a match quality of <40 were automatically deleted. For each of the remaining peaks, the mass spectra were manually examined and the identification was confirmed. In cases where it was difficult to confirm identification of a compound, the three best possible hits were considered. Match quality >40 is not considered a basis for identification in conventional GC-MS studies; but in the analysis of complex combustion emission, a match quality >40 is advancement over previous separation and identification procedures. The focus of the analysis was to identify any

potentially toxic compounds that might not have been identified due to lack of separation.

Once the peaks obtained from MDGC analysis were tentatively identified, the compounds of interest were selected. The identity and quantification of these selected compounds were then confirmed using conventional scanning or selected ion techniques. For example, MDGC-MS showed the presence of bis-phenol A (BPA) and dioctyl phthalate [bis(2-ethylhexyl)phthalate] in the samples; therefore, BPA and dioctyl phthalate were used as target compounds in conventional gas chromatography/mass spectrometry (GC-MS) analysis. The conventional GC-MS analyses of the household waste and diesel particulate samples were performed in a Varian Saturn 2000 Ion Trap. The separation was performed using conventional, temperature-programmed GC-MS (40–300 °C at a rate of 20 °C min^{-1}) and a DB-5MS column (J&W Scientific). Since only

Table 2
Compounds identified in the DRI diesel particulate extract and their respective emission rates

Library/ID	Emission rate (μg mile^{-1})	Match quality	CAS #
Methyl cyclohexanone	21.87	90	583-60-8
2H-1,4-benzoxazine, 3,4-dihydro-	2.34	87	5735-53-5
2,5-Heptadien-4-one, 2,6-dimethyl-	39.82	91	504-20-1
4-Piperidinone, 2,2,6,6-tetramethyl	110.99	81	826-36-8
1-Naphthalenol, 4-methoxy	2.73	47	84-85-5
Naphthalene, 1-ethoxy	1.34	49	5328-01-8
[1,1′-Biphenyl]-4,4′-diol	0.47	47	98-88-6
1H-Isoindole-1,3(2H)-dione	4.44	78	85-41-6
Benzofuran	1.04	76	271-89-6
Ionol 2	1.46	87	4130-42-1
Benzoic acid, 4-hydroxy-	4.29	91	99-96-7
2-Naphthalenecarboxylic acid	18.48	95	93-09-4
9H-Fluoren-9-one	7.17	95	486-25-9
Ethanedione, (4-methylphenyl)phenyl	6.08	72	2431-00-7
1,1′-Biphenyl, 2-carboxylic acid	1.86	87	947-84-2
9(10H)-Anthracenone	4.19	83	90-44-8
9H-Xanthen-9-one	12.35	90	90-47-1
1H-Phenalen-1-one	13.44	94	548-39-0
9,10-Anthracenedione	24.88	95	84-65-1
Cyclopenta(def)phenanthrenone	10.02	94	5737-13-3
Fluoranthene	145.01	93	206-44-0
Pyrene	125.78	90	129-00-0
Phenindione	6.71	90	83-12-5
11H-Benzo[b]fluorine	46.72	91	243-17-4
1,1′:2′,1″-terphenyl	5.50	87	84-15-1
7H-Benz[de]anthracen-7-one	7.39	96	82-05-3
Triphenylene	23.04	89	217-59-4
1,2′-Binaphthalene	2.45	86	4325-74-0
Chrysene, 6-methyl-	5.67	90	1705-85-7
Benz[a]anthracene-7,12-dione	1.64	93	2498-66-0
Benzo[k]fluoranthene	15.31	93	207-08-9
Chrysophanol	0.96	64	481-74-3
Benzo[a]pyrene	13.44	93	50-32-8

internal standards were used in MDGC-MS to quantify the target analyses, external standards were used in the conventional GC-MS analyses. High-purity BPA and dioctyl phthalate (more than 99% and 99%, respectively, obtained from Aldrich) were used to prepare the external standards. However, due to the great complexity of the samples, an ion extraction was also required to identify the compounds. Ion 213 for BPA and 149 for the dioctyl phthalate were used for quantification. An internal standard of deuterated polycyclic aromatic hydrocarbons (PAHs)(US-108-N Ultra Scientific) was also added to verify the reliability of the autosampler, and a replicate of each concentration was also prepared to verify that the injection volume was constant. The domestic waste combustion sample had to be diluted by a factor of 10 to fall within the external standard calibration for BPA. The diesel combustion sample was not diluted.

In this study, compounds of primary importance were the oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) as well as chlorine- and bromine-containing ringed compounds. Because of their polarity, these peaks are often found near the end of the heartcuts and are therefore easy to locate in the chromatogram. Another important aspect taken into consideration during data analysis was the possibility of multiple peaks with the same library identification. During the trap and release process, it is possible for a component to be split into zones. One section of the component may be released, while the other remains trapped in the column. The second section is then released in the following heartcut, making it possible to have identical library hits for peaks in sequential heartcuts. Legitimate multiple identifications were verified by finding the difference in the peak retention times. Multiple peaks of the same compound should be 45 s apart, the equivalent length of one heartcut. The total area response for compounds with multiple peaks was calculated by adding the areas of all the peaks. Once the data for each sample had been reduced to a manageable amount, the concentrations of each component were approximated using internal standards. The internal standard mixture contained six different compounds; the one closest to the original sample component retention time was used to calculate the concentration.

3. Results and discussion

The combustion samples analyzed in this study were very complex. The difficulty in identifying and quantifying compounds was not only due to the complex sample matrix, but also because the concentration of the compounds was extremely low, in the range of $1–5 \, ng \, ml^{-1}$. MDGC was able to separate low-concen-

tration oxygenated-PAHs from the high-concentration compounds. This increased separation was helpful in accurate identification and calculation of pollutant concentrations and emission rates. A detailed description of the MDGC-MS analyses of both diesel particle extracts and the uncontrolled domestic waste burn sample is given in the thesis of Klosterman, 2002.

MDGC-MS analyses showed that both the EPA and DRI diesel extracts contained PAHs, oxy-PAHs and nitrated-PAHs. Some of the oxy-PAHs observed in diesel particulate exhaust are shown in Fig. 3. The reason for showing only oxy-PAHs is that they show a structural resemblance to known EDCs such as parabens, alkyl phenols, and bisphenols. Several compounds with structural similarities to known and suspected EDCs were observed in both DRI and EPA diesel combustion samples and could be responsible for the observed overall estrogenic and antiestrogenic activity of diesel particulate extract (Taneda et al., 2002; Tsukue et al., 2001; Watanabe and Oonuki, 1999). Although structural similarities do not necessarily translate into estrogenic activity (Elsby et al., 2000), the existence of these compounds warrants additional identification and testing from a variety of combustion sources. Some of the oxy-PAHs shown in Fig. 3 were also observed in MDGC-MS analyses of the polar fraction of the emissions collected from reformulated gasoline combustion along with two known EDCs-alkyl phenols and bisphenol A (Klosterman, 2002).

Table 2 shows a list of suspected EDCs identified in the DRI sample, along with their approximate emission rates. As can be seen from this table, some of these

Table 3
Compounds identified in the EPA diesel particulate extract

| Library identification	Concentration ppm (ng µL^{-1})	CAS #
C1 phenol	0.21	95-48-7
C2 phenol	0.15	90-00-6
m-Ethoxybenzaldehyde	1.98	22924-15-8
Benzyl alcohol	1.14	100-51-6
2-Hydroxy-benzaldehyde	5.24	90-02-8
Acetophenone	2.17	98-86-2
2-Hydroxy-3-methylbenzaldehyde	0.51	824-42-0
Benzoic acid	4.23	65-85-0
1,3-Isobenzofurandione	0.52	85-44-9
1-Naphthalenol	0.14	90-15-3
1,4-Naphthalenedione	0.81	130-15-4
2-Nitro-1-naphthol	0.52	607-24-9
9H-fluoren-9-one	0.73	486-25-9
1-Phenanthrenol	0.28	2433-56-9
9(10H)-anthracenone	0.47	90-44-8
1H-phenalen-1-one	0.16	548-39-0
2,8-Dimethyldibenzothiophene	0.41	1207-15-4
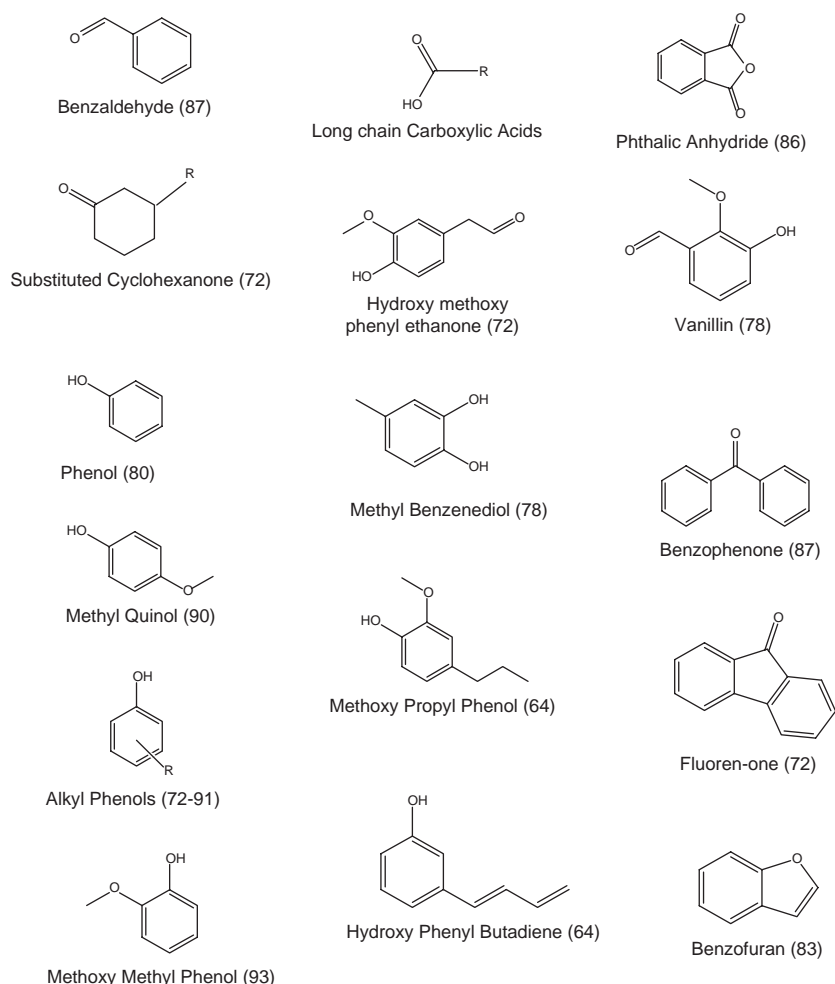
Fig. 4. Compounds identified from the MDGC-MS analysis of the uncontrolled domestic waste burn sample.

oxygenated compounds have significant emission rates. A list of suspected EDCs from the EPA diesel extract is shown in Table 3. The EPA diesel particulate sample was collected from an idling truck, so no emission rate per kilometer could be calculated for these compounds. The data in Tables 2 and 3 cannot be compared because the data shown in these two tables were collected from two different engines burning diesel fuel from different sources and operating under different conditions. Also two different extraction techniques were used.

MDGC-MS analysis of combustion emissions from uncontrolled domestic waste burning yielded 955 separate peaks. Some of these 955 peaks were duplicates because MDGC analysis can identify the same component in two different portions of the chromatogram, 45 s apart. Examples of some of the oxy-PAHs and PAHs observed in barrel burn samples are shown in Fig. 4. Since this was the first attempt to look for EDCs in the

barrel burn samples, the presence of known oxygenated EDCs like BPA, dioctyl phthalate, alkyl phenols, and parabens, was also investigated. BPA and dioctyl phthalate was expected since these compounds are used as plasticizers in domestic plastic products.

The MDGC analyses of the emissions from uncontrolled burning of domestic waste showed that both BPA and dioctyl phthalate were present at significant concentrations. Other possible EDCs, notably tribromophenol and oxygenates, and their emission factors are shown in Table 4. The emission factors of many of these oxygenated compounds (some suspected EDCs) are higher than the emission factors of known pollutants like anthracene and dimethyldibenzothiophene. To determine the total oxygenate content of the domestic waste burn sample, compounds with names containing characters -oxy- or -al-, or -ol- or -one- were extracted from the list, totaling 468 of the 955 compounds. While

Table 4
List of compounds identified in the open-air barrel burn sample and their respective emission rate

Library identification	Concentration ppm (ng μL^{-1})	Emission Rate (mg kg^{-1})	CAS #
Bisphenol A	58.3	9.66	80-05-7
Dioctyl phthalate	2031.0	336.35	117-81-7
C3 phenol	20.4	3.38	644-35-9
2-Methoxy phenol	99.4	16.46	90-05-1
1-Naphthalenol	22.9	0.40	90-15-3
Benzaldehyde	35.24	5.84	100-52-7
5-Methyl furfural	46.86	7.76	620-02-0
Benzofuran	19.14	3.17	271-89-6
Benzaldehyde, 2-hydroxy-	7.13	1.18	90-02-8
Ethanone, 1-phenyl-	25.48	4.22	98-86-2
1,2-Benzenediol	80.39	13.31	120-80-9
Benzoic acid	28.38	4.70	65-85-0
2,3-Dimethoxytoluene	1.72	0.28	4463-33-6
1H-inden-1-one, 2,3-dihydro-	9.77	1.62	83-33-0
4-Methyl catechol	18.08	2.99	452-86-8
5-Acetoxymethyl-2-furaldehyde	3.43	0.57	10551-58-3
1,3-Isobenzofurandione	22.84	3.78	85-44-9
Phenol, 2,6-dimethoxy-	4.09	0.68	91-10-1
Benzaldehyde, 4-hydroxy-3-methoxy-	44.49	7.37	18278-34-7
Biphenylene	33.79	5.60	259-79-0
Dibenzofuran	17.42	2.89	132-64-9
Benzoic acid, 4-hydroxy-3-methoxy-	7.92	1.31	121-34-6
Phenol, 2,4,6-tribromo-	27.85	4.61	118-79-6
Methanone, diphenyl-	13.73	2.27	119-61-9
[1,1′-Biphenyl]-4-carboxaldehyde	5.41	0.90	3218-36-8
1,1-Diphenylpropene	11.22	1.86	833-81-8
9H-fluoren-9-one	22.04	3.65	486-25-9
Anthracene	39.07	6.47	120-12-7
1,4-Benzenedicarboxylic acid	3.30	0.55	100-21-0
1H-phenalen-1-one	4.75	0.79	548-39-0
9,10-Anthracenedione	1.72	0.28	84-65-1
2,8-Dimethyldibenzothiophene	3.70	0.61	1207-15-4
Fluoranthene	18.74	3.10	206-44-0
Pyrene	8.58	1.42	129-00-0
1,1′:4′,1″-Terphenyl	23.10	3.83	92-94-4
11H-benzo[b]fluorine	8.84	1.46	243-17-4
Triphenylene	13.46	2.23	217-59-4
7H-benz[de]anthracen-7-one	4.22	0.70	82-05-3
Benzo[k]fluoranthene	11.75	1.95	207-08-9
Benzo[e]pyrene	6.60	1.09	192-97-2

some misidentifications are inevitable when using automated routines, the identification confidence can be improved by selecting only the compounds with match qualities $\geqslant 70$ (out of 100). The number of oxygenated compounds over 70% match quality by MDGC-MS is 180 of the original 955 (excluding duplicate identifications). The pie charts in Fig. 5 clearly illustrate that oxygenate compounds are a significant fraction of domestic waste combustion emissions. The majority of these oxygenate compounds are highly polar and are not separated or targeted (ion extraction) during conventional GC-MS.

Four of the MDGC-identified oxygenate compounds in the emissions from the open-air domestic waste barrel burns (Table 4) are listed as suspected EDCs (Endocrine Toxicant list on ED Scorecard), and seven of the compounds are listed on the Toxic Release Inventory (TRI) list (EPCRA 313). In order to establish a preliminary, single-run estimate of TRI emissions from barrel burns, the Table 4 emission factors were combined with EPA estimates for barrel burn activity (Environmental Defense, 2003). The barrel burn activity is based on the estimate that 52.7 million people live in US non-metropolitan areas (NMA) and produce 388 kg

of waste per person per year and 40% of this waste in NMA is burned in backyard barrels. The calculated emission factor values were compared with the TRI-reported air emissions from industry (year 2000) in Table 5 to provide a perspective on the magnitude of barrel burn TRI emissions. The barrel burn oxygenates are a significant fraction of the value estimated for

(a) **Match Quality for all Peaks**

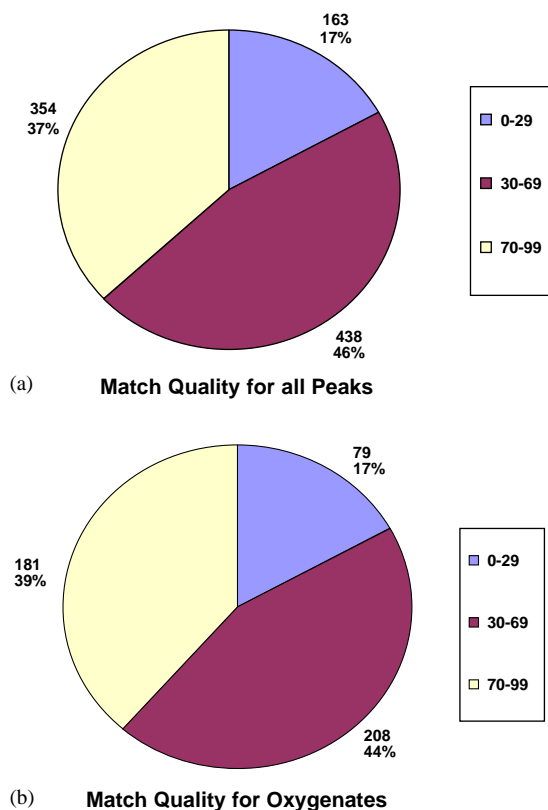(b) **Match Quality for Oxygenates**

Fig. 5. Match quality of automated identifications from domestic waste combustion sample (a) all compounds and (b) oxygenated compounds.

industrial oxygenate emissions. Although considerable uncertainty exists in the barrel burn TRI compound emission estimates due to the limited number of trials, this comparison does suggest that uncontrolled domestic waste burning may be a significant source of these specific TRI compound emissions.

The results of this study show that emissions of oxy-PAHs are comparable to PAHs and just like PAHs, these oxy-PAHs are present in combustion emission samples collected from very different types of combustion processes. A close examination of the kinetic formation mechanisms of PAHs and PCDDs/Fs shows that plausible reaction pathways for formation of oxy-PAHs are present in all combustion processes (Richter and Howard, 2000; Sidhu, 1999). All combustion processes generate hydrocarbon (e.g., C_3H_3, CH_3) and oxy-hydrocarbon (e.g., CHO, C_6H_5O) radicals along with combustion radicals like H, OH, HO_2, and O. The interactions amongst these radicals, or radical-molecule interactions, can easily lead to formation of oxygenated PAHs like the ones observed in this study. In fact, it will be easier to form oxygenated PAHs than chlorinated EDCs like PCDDs/Fs because the oxygenated PAHs formation requires one less mechanistic step, specifically chlorination (Sidhu, 1999).

In addition to domestic waste combustion emissions studied here, the presence of BPA and brominated BPA were also observed during the incineration/thermal decomposition study of epoxy circuit board material, which is highly brominated (Striebich and Rubey, 1990). These studies were conducted in our laboratory over a temperature range of 300–800 °C under oxidative and pyrolytic conditions. Other compounds formed in this study (Striebich and Rubey, 1990) included brominated phenols. Results from combustion of cabling materials (sheaths and insulators that surround cables) and brominated flame retardant also indicate formation of brominated dibenzodioxins (Dellinger et al., 1993; Striebich et al., 1991). In addition to these cited laboratory studies, MDGC analyses of a hazardous

Table 5
Comparison of TRI emissions from barrel burns with the top (N) industry sectors

TRI compound	CAS #	Barrel burn emissions (kg year^{-1})	Industry emissions (kg year^{-1})
Bisphenol A, 4,4′-isopropylidenediphenol	80-05-7	79,000	72,000 (7)
Dioctyl phthalate, Di(2-ethylhexyl)phthalate (DEHP)	117-81-7	2,751,000	114,000 (16)
Ethanone, 1-phenyl-; acetophenone	98-86-2	34,500	70,000 (8)
1,2-Benzenediol; catechol	120-80-9	109,000	4000 (3)
1,3-Isobenzofurandione, phthalic anhydride	85-44-9	31,000	111,000 (6)
Dibenzofuran	132-64-9	24,000	15,000 (4)
Anthracene	120-12-7	53,000	12,000 (5)

waste incinerator emission sample also show the presence of nitrated-PAHs, chlorinated PAHs, brominated phenols, and brominated ethers as well as several oxygenated aromatic hydrocarbons, including known EDCs alkyl phenols and bisphenol A (Klosterman, 2002).

4. Conclusions

Increase in resolution obtained by using the MDGC-MS technique helped in identifying and quantifying various classes of PAHs in effluent stream of both controlled (diesel engine) and uncontrolled (barrel burn) combustion sources. Significant emissions of known and suspected EDCs were observed from uncontrolled domestic waste burn and diesel engine samples. The results of laboratory and field studies combined with kinetic/mechanistic observations suggest that EDCs or suspected EDCs can form during various combustion processes. This suggests a need to better characterize combustion emissions and also to develop an emission-factor database for several known and suspected combustion-generated EDCs. Further analysis of combustion emissions, such as that provided by the MDGC technique, may result in the identification of additional EDCs, and will be necessary for an assessment of the overall impact of combustion-generated EDCs on human and environmental health.

Acknowledgments

References

Arnold, S.F., Robinson, M.K., Notides, A.C., Guillette Jr., L.J., McLachlan, J.A., 1996. A yeast estrogen screen for examining the relative exposure of cells to natural and xenoestrogens. Environmental Health Perspectives 104, 544–548.

Colborn, T., Clement, C., 1992. Chemically induced alterations in sexual and functional development: the wildlife/human connection. In: Advances in Modern Environmental Technology. Princeton Scientific Publishing, Princeton, NJ.

Colborn, T., Vom Saal, F.S., Soto, A.M., 1993. Developmental effects of endocrine-disrupting chemicals in wildlife and humans. Environmental Health Perspectives 101, 378–384.

Crews, D., Bergeron, J.M., McLachlan, J.A., 1995. The role of estrogen in turtle sex determination and the effect of PCBs. Environmental Health Perspectives 103 (Suppl 7), 73–77.

Cummings, A.M., Metcalf, J.L., 1995. Methoxychlor regulates rat uterine estrogen-induced protein. Toxicology and Applied Pharmacology 130, 154–160.

Dellinger, B., Taylor, P.H., Tirey, D.A., 1991. Minimization and control of hazardous combustion byproducts. EPA/600/S2-90/039 [NTIS PB90-259854].

Dellinger, B., Maqsud, L., Sidhu, S.S., 1993. Kinetics of toxic combustion by-product formation during brominated flame retardant incineration. Organohalogen Compounds 11, 261–264.

Elsby, R., Ashby, J., Sumpter, J.P., Brooks, A.N., Pennie, W.D., Maggs, J.L., Lefevre, P.A., Odum, J., Beresford, N., Paton, D., Park, B.K., 2000. Obstacles to the prediction of estrogenicity from chemical structure: assay-mediated metabolic transformation and the apparent promiscuous nature of estrogen receptor. Biochemical Pharmacology 60, 1519–1530.

Environmental Defense, 2003. Scorecard website (accessed March 2003) http://www.scorecard.org/chemical-profiles/index.tcl

Fiedler, H., 1993. Formation and sources of PCDD/PCDF. Organohalogen Compounds 11, 221–228.

Guillette, L.J., Pickford, D.B., Crain, D.A., Roney, A.A., Percival, H.F., 1995. Organization versus activation—the role of endocrine-disrupting contaminants (EDCs) during embryonic-development in wildlife. Environmental Health Perspectives 103 (Suppl 7), 157–164.

Gullett, B., Lemieux, P., Lutes, C., Winterrowd, C., Winters, D., 2001. Emissions of PCDD/F from uncontrolled, domestic waste burning. Chemosphere 43, 721–725.

Gullett, B.K., Ryan, J.V., 2002. On-road emissions of PCDDs and PCDFs from heavy duty diesel vehicles. Environmental Science and Technology 36, 3036–3040.

Gullett, B.K., Lemieux, P.M., Dunn, J.E., 1994. Role of combustion and sorbent parameters in prevention of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran formation duringwaste combustion. Environmental Science and Technology 28, 107–118.

Harris, C.A., Henttu, P., Parker, M.G., Sumpter, J.P., 1997. The estrogenic activity of phthalate esters in vitro. Environmental Health Perspectives 105, 802–811.

Harrison, R.M., Deacon, A.R., Jones, M.R., Appleby, R.S., 1997. Sources and processes affecting concentrations of PM_{10} and $PM_{2.5}$ particulate matter in Birmingham (UK). Atmospheric Environment 31, 4103–4117.

Kinghorn, R.M., Marriot, P.J., 1998. Enhancement of signal-to-noise ratios in capillary gas chromatography by using a longitudinally modulated cryogenic system. Journal of High Resolution Chromatography 21, 32–38.

Klosterman, J.R., 2002. Analysis of complex combustion mixtures using multidimensional gas chromatography mass spectrometry (MDGC-MS). M.S. Thesis, University of Dayton, Dayton, OH.

Konduri, R., Altwicker, E., 1994. Analysis of time scales pertinent to dioxin furan formation on fly ash surfaces in municipal solid waste incinerators. Chemosphere 28, 23–45.

Lemieux, P.M., Lutes, C.C., Abbott, J.A., Aldous, K.M., 2000. Emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from the open burning of household waste in barrels. Environmental Science and Technology 34, 377–384.

Lenoir, D., Wehrmeier, A., Kaune, A., Zimmerman, R., Taylor, P.H., Sidhu, S.S., 1998. Thermal formation of polychlorinated dibenzo-*p*-dioxins and-furans: investigations on relevant pathways. Environmental Engineering Science 15, 37–47.

Lenoir, D., Wehrmeier, A., Sidhu, S.S., Taylor, P.H., 2001. Formation and inhibition of chloroaromatic micropollutants formed in incineration processes. Chemosphere 43, 107–114.

Marriot, P.J., Kinghorn, R.M., 1997. Longitudinally modulated cryogenic system. A generally applicable approach to solute trapping and mobilization in gas chromatography. Analytical Chemistry 69, 2582–2588.

Mori, Y., Taneda, S., Hayashi, H., Sakushima, A., Kamata, K., Suzuki, A., Yoshino, S., Sakata, M., Sagai, M., Seki, K., 2002. Estrogenic activities of chemicals in diesel exhaust. Biological and Pharmaceutical Bulletin 25, 145–146.

Oppelt, E.T., 1986. Hazardous waste destruction. Environmental Science and Technology 20, 312–318.

Richter, H., Howard, J.B., 2000. Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways. Progress in Energy and Combustion Science 26, 565–608.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1993. Sources of fine organic aerosol. 2. Non-catalyst and catalyst equipped automobiles and heavy-duty diesel trucks. Environmental Science and Technology 27, 636–651.

Routledge, E.J., Sumpter, J.P., 1996. Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast. Environmental Toxicology and Chemistry 15, 241–248.

Rubey, W.A., Striebich, R.C., Ryan J., 1999. Analysis of trace-level organic combustion process emissions using novel multidimensional gas chromatography-mass spectrometry (MDGC-MS) procedures. Proceedings of the International Conference on Incineration and Thermal Treatments, Orlando, FL.

Ryan, J.V., Lemieux, P.M., Lutes, C., Tabor, D., 1996. Development of PIC target analyte list for hazardous waste incineration processes. Proceedings of the International Incineration Conference, Savannah, GA, pp. 445–454.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R., 1999. Measurement of emissions from air pollution sources. 2. C_1 through C_{30} organic compounds from medium duty diesel trucks. Environmental Science and Technology 33, 1578–1587.

Sidhu, S.S., 1999. Role of aliphatic precursors in the formation mechanism of PCDD/F, PCB AND PCN. Organohalogen Compound 41, 59–62.

Sidhu, S.S., Maqsud, L., Dellinger, B., 1995. The homogeneous gas-phase formation of chlorinated and brominated dibenzo-*p*-dioxin from 2,4,6-trichlorophenol and 2,4,6-tribromophenol. Combustion and Flame 100, 11–20.

Soto, A.M., Chung, K.L., Sonnenschein, C., 1994. The pesticides endosulfan, toxaphene, and dieldrin have estrogenic effects on human estrogen-sensitive cells. Environmental Health Perspectives 102, 380–383.

Soto, A.M., Sonnenschein, C., Chung, K.L., Fernandez, M.F., Olea, N., Olea-Serrano, F., 1995. The E-screen assay as a tool to identify estrogens—an update on estrogenic environmental pollutants. Environmental Health Perspectives 103, 113–122.

Stone, R., 1994. Environmental estrogens stir debate. Science 265, 308–310.

Striebich, R., Rubey, W., 1990. A system for thermal diagnostic studies. American Laboratory 2 (1), 64–67.

Striebich, R., Rubey, W., Tirey, D., Dellinger, B., 1991. High-temperature degradation of polybrominated flame retardant materials. Chemosphere 23, 1197–1204.

Striebich, R.C., Rubey, W.A., Klosterman, J., 2002. Trace level measurements of complex combustion effluents and residues using multidimensional gas chromatography mass spectrometry (MDGC-MS). Waste Management 22, 413–420.

Taneda, S., Hayashi, H., Sakushima, A., Seki, K., Suzuki, A., Kamata, K., Sakata, M., Yoshino, S., Sagai, M., Mori, Y., 2002. Estrogenic and antiestrogenic activities of two types of diesel exhaust particles. Toxicology 170, 153–161.

Tsukue, N., Toda, N., Tsubone, H., Sagai, M., Jin, W., Watanabe, G., Taya, K., Birumachi, J., Suzuki, A., 2001. Diesel exhaust (DE) affects the regulation of testicular function in male Fischer 344 rats. Journal of Toxicology and Environmental Health Part A 63, 115–126.

Venkataraman, C., Friedlander, S.K., 1994. Size distributions of polycyclic aromatic-hydrocarbons and elemental carbon. 2. Ambient measurements and effects of atmospheric processes. Environmental Science and Technology 28, 563–572.

Watanabe, N., Oonuki, Y., 1999. Inhalation of diesel engine exhaust affects spermatogenesis in growing male rats. Environmental Health Perspectives 107, 539–544.

Zacharewski, T., 1997. In vitro bioassays for assessing estrogenic substances. Environmental Science and Technology 31, 613–623.

Zielinska, B., Sagebiel, J.C., 2001. Collection of in-use mobile source emissions samples for toxicity testing, NREL Project #RCI-8-18148-01, Final Report.